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Observation of positional disorder in $LiNaSO_4$ crystals by the electron spin resonance of the $SO_4{}^-$ free radicals

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Paramagnetic $SO_4{}^-$ free radicals produced in pure $LiNaSO_4$ crystals and in $LiNaSO_4$ crystals doped with $CrO_4{}^{2-}$, Cd^{2+}, and Mg^{2+} were detected by electron spin resonance (ESR) at room temperature and at low temperatures. Both the $SO_4{}^-$ centers of axial symmetry and of orthorhombic symmetry are observed. It is established through the ESR of the orthorhombic $SO_4{}^-$ centers that a small fraction of the sulfate oxygens is positionally disordered, and the ESR spectra can be fitted by assuming that the disordered sulfate group is related to the main group by reflections about the $\{11\bar{2}0\}$ planes or by two-fold rotations about the $\langle 11\bar{2}0\rangle$ axes. Observations by polarized light and by chemical etching does not reveal any twin-domain structure in the $LiNaSO_4$ sample crystals. Consequently, the disorder is randomly and uniformly distributed at equivalent positions in the crystal lattice. It is also established by ESR that the $SO_4{}^-$ free radicals of orthorhombic symmetry are most likely to be associated with local Na^+ vacancies produced mainly by radiation damage, and that the lowering of the molecular symmetry from axial to orthorhombic is not intrinsic.

I. INTRODUCTION

This paper reports the electron spin resonance (ESR) of the $SO_4{}^-$ centers in single crystals of γ-ray-irradiated $LiNaSO_4$ crystals. We shall report the effect of impurities on the production and the magnetic symmetry of the $SO_4{}^-$ centers, and the use of the $SO_4{}^-$ free radicals as ESR probes to investigate the disorder in the atomic positions of the sulfate oxygens. There is at present no report of the observation of positional disorder in $LiNaSO_4$ crystals,[1-3] however, the Raman spectra at high temperatures indicate that the orientational disorder of the sulfate ions increases with temperature.[4] The study of positional disorder is of much current interest.[5-8] One advantage of ESR in the analysis of positional disorder in crystalline solids is that the ESR spectra arising from the orientationally disordered atoms are separable. The ESR method can provide direct and unambiguous evidence of positional disorder. The observations of twin domains (which is a special case when the orientational disorder has aggregated into macroscopic regions) by ESR have been reported in the past,[9-12] but to our knowledge, there is no report of the detection by ESR of positional disorder randomly distributed at equivalent positions in the crystal lattice.

$LiNaSO_4$ is a member of the crystals of alkali double sulfates having the general formula of $LiMSO_4$, where M stands for Na, K, Rb, Cs, and $NH_4{}^+$, and there is an abundance of positional disorder in these crystals. Crystals of $LiRbSO_4$,[13] $LiCsSO_4$,[14] and $LiNH_4SO_4$ (Ref. 15) are usually twinned. The kinds of positional disorder that could exist in crystalline solids are exemplified by the various models proposed to account for the room-temperature x-ray diffractions of $LiKSO_4$ crystals. Both the models of the random distribution[8,16] and the ordered distribution[6,7] (twin domains) of the static disorder in the positions of the sulfate oxygens have been proposed. Dynamical disorder in the sulfate oxygens has also been proposed for the room-temperature structure of $LiKSO_4$.[5]

ESR of SO_4^- in single crystals have been reported in K_2SO_4,[17-19] Na_2SO_4,[20] $LiNaSO_4$,[21] $LiKSO_4$,[12,22-23] and $K_3Na(SO_4)_2$.[24] The $SO_4{}^-$ free radical is identified by ESR from its g values.[17-18] The magnetic symmetry, and hence the molecular symmetry of the $SO_4{}^-$ free radicals produced by ionizing radiation are usually lower than the molecular symmetry of the $SO_4{}^{2-}$ in the crystal lattice. Several models have been proposed to explain this lowering of the magnetic symmetry, and these includes(1) static Jahn-Teller distortion or crystal-field distortion,[25](2) an intrinsic property,[26] and (3) association with local cation vacancies[18-19] (which can be included in the category of crystal-field distortion). To test these models, we feel that it is best to choose host crystal lattices in which the molecular symmetry of the $SO_4{}^{2-}$ ions is high, since any departure of the $SO_4{}^-$ free radicals from the molecular symmetry of the $SO_4{}^{2-}$ ions can be definitely established by ESR. Double sulfates of the Langbeinite $K_2Mg_2(SO_4)_3$ structure are cubic crystals,[27] but sulfur atoms occupy general positions in the crystal lattice, and the molecular symmetry of the sulfate ions is low. Four crystals of sulfates are uniaxial: $LiKSO_4$ is hexagonal,[7,28] and $LiNaSO_4$,[1] $K_3Na(SO_4)_2$, and $KNaSO_4$ (Ref. 29) are trigonal. The molecular symmetry of the $SO_4{}^{2-}$ ions is C_{3v} in these four crystals, and the symmetry axis of the sulfate tetrahedra coincides with the c axis. These crystals seem to be ideal for the study of the molecular symmetry of the $SO_4{}^-$ free radicals. The ESR of $SO_4{}^-$ centers in pure and x-irradiated $LiNaSO_4$ crystals have been reported,[21] but the analysis of the ESR spectra was questioned.[30,31] We shall report in this paper the analysis of the ESR of the $SO_4{}^-$ centers produced by γ irradiation in pure $LiNaSO_4$

crystals and in $LiNaSO_4$ crystals doped with CrO_4^{2-}, Cd^{2+}, and Mg^{2+}. The CrO_4^{2-} ions, which are efficient electron trap centers,[32,33] can increase the yield of stable SO_4^- centers.[12] Cd^{2+} and Mg^{2+} are chosen as dopants because its ionic radii are nearly identical to those of the Na^+ and the Li^+ ions. The purpose of the doping of impurities is to test the model of the association of the SO_4^- free radicals with local cation vacancies.

II. EXPERIMENTAL

Single crystals of pure $LiNaSO_4$ for ESR study were grown at 40 and 60 °C from aqueous solutions containing equimolar quantities of lithium sulfate monohydrate and sodium sulfate. $LiNaSO_4$ crystals doped with CrO_4^{2-}, Cd^{2+}, and Mg^{2+} impurities were grown by adding a small amount of Na_2CrO_4, $3CdSO_4 \cdot 8H_2O$, and $MgSO_4 \cdot 7H_2O$, respectively, into the growth solutions. The x-ray diffraction patters of powdered crystals confirms the $P31c$ structure[1] of our sample crystals. The a axis of the sample crystals was identified by single-crystal x-ray diffraction. Sample crystals were irradiated at ambient temperatures with γ rays from a Co^{60} source for total dosages of 2–3 Mrad. The ESR spectrometer used has been described elsewhere.[12]

III. CRYSTAL STRUCTURE OF $LiNaSO_4$

$LiNaSO_4$ crystals are of the trigonal $P31c$ structure, and the lattice constants are $a = 7.6270$ Å and $c = 9.8579$ Å.[1] There are six molecular units in a hexagonal unit cell. The Li atoms and the Na atoms occupy general positions, and the sulfur atoms are located on two different threefold axes. There are three crystallographically inequivalent sulfate tetrahedra: $(SO_4)_1$ is slightly elongated, $(SO_4)_2$ is slightly compressed, and $(SO_4)_3$ is nearly regular. The sulfate tetrahedra are of the C_{3v} molecular point-group symmetry, and the point symmetry at the sulfur sites is the threefold axis. Figure 1 shows the projections of the atomic positions onto a (0001) plane of the crystal lattice.

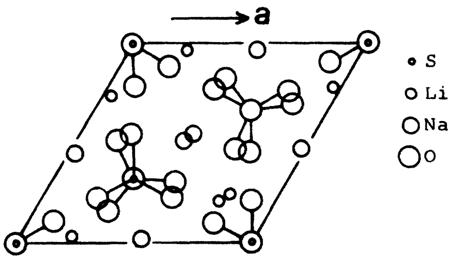

FIG. 1. Projections of the atomic positions of $LiNaSO_4$ onto a (0001) plane.

IV. ANALYSIS OF THE ESR OF THE SO_4^- CENTERS

Paramagnetic SO_4^- radicals are spin (effective spin) -$\frac{1}{2}$ centers, and the effective g factors can be fitted by the equation,[34,35]

$$R = (l^2 T_{xx} + m^2 T_{yy} + n^2 T_{zz} + 2lm T_{xy} + 2mn T_{yz} + 2nl T_{zx})^{1/2} , \tag{1}$$

where R is the effective g factor, T_{ij} are the elements of the T matrix which is the square of the g matrix, and l, m, and n are the directional cosines of the magnetic field with respect to the reference x, y, and z axes which are chosen parallel to the a, b^*, and c axes of the crystal lattice. The b^* axis is perpendicular to both the a and the c axes. It is convenient to define two lines in a rotation pattern (the point diagram of the values of the resonance field versus the orientation of the magnetic field) as magnetic conjugates when their g factors in a general $\xi\eta$ plane are given, respectively, by

$$R = [\cos^2\varphi \, T_{\xi\xi} + \sin^2\varphi \, T_{\eta\eta} \pm \sin(2\varphi) T_{\xi\eta}]^{1/2} , \tag{2}$$

TABLE I. The T matrix, the principal g values, and the principal axes. RT denotes room temperature.

Center		T matrix		Principal values and axes
A	4.0173	0.0111	0.0081	2.0037: [0.9641, −0.2553,0.0733]
(RT)	0.0111	4.0731	0.0563	2.0078: [0.2459,0.7535, −0.6097]
	0.0081	0.0563	4.1041	2.0368: [0.1004,0.6058,0.7892]
B	4.0315	0.0273	0.0244	2.0032: [0.6954,0.1521, −0.7024]
(RT)	0.0273	4.1287	0.0521	2.0080: [−0.6705,0.4893, −0.5578]
	0.0244	0.0521	4.0483	2.0405: [0.2588,0.8588,0.4422]
C	4.0251	−0.0083	0.0106	2.0050: [0.9356,0.2460,0.2531]
(200 K)	−0.0083	4.0471	−0.0044	2.0113: [−0.0916,0.8619,0.4988]
	0.0106	−0.0044	4.0550	2.0154: [0.3408, −0.4435,0.8290]
D	4.0816	0	0	
(200 K)	0	4.0816	0	$g_{\parallel} = 2.0179$, $g_{\perp} = 2.0203$
	0	0	4.0719	
E	4.0288	0.0445	0.0121	2.0030: [0.7775, −0.4210,0.4672]
(120 K)	0.0445	4.2398	0.1313	2.0804: [0.1462,0.8435,0.5168]
	0.0121	0.1313	4.1102	2.0097: [−0.6116, −0.3335,0.7174]

where φ is the angle between the field direction and the ξ direction. A pair of conjugate lines arise from two chemically equivalent but magnetically inequivalent sites, and their rotation patters are symmetrical to each other.

The point group of the $P31c$ (C_{3v}^4) structure of $LiNaSO_4$ is the trigonal $31m$ group, which is of the same Laue-symmetry class as the trigonal 312 (D_3) group. ESR of spin-$\frac{1}{2}$ centers cannot distinguish between these two symmetry groups. The T matrices of the magnetically inequivalent sites are related by similarity transformations.[36] The six T matrices pertaining to the $31m$ (or the 312) group are the following (upper signs):

$$T_1=\begin{bmatrix} xx & \pm xy & \pm xz \\ \pm xy & yy & yz \\ \pm xz & yz & zz \end{bmatrix}, \quad T_2=\begin{bmatrix} xx & \mp xy & \pm xz \\ \mp xy & yy & yz \\ \pm xz & yz & zz \end{bmatrix},$$

$$T_3=\begin{bmatrix} \frac{1}{4}xx+\frac{3}{4}yy-\frac{\sqrt{3}}{2}xy & \frac{\sqrt{3}}{4}(xx-yy)-\frac{1}{2}xy & \pm\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz \\ \frac{\sqrt{3}}{4}(xx-yy)-\frac{1}{2}xy & \frac{3}{4}xx+\frac{1}{4}yy+\frac{\sqrt{3}}{2}xy & \mp\frac{1}{2}yz\mp\frac{\sqrt{3}}{2}xz \\ \pm\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz & \mp\frac{1}{2}yz\mp\frac{\sqrt{3}}{2}xz & zz \end{bmatrix},$$

$$T_4=\begin{bmatrix} \frac{1}{4}xx+\frac{3}{4}yy+\frac{\sqrt{3}}{2}xy & \frac{\sqrt{3}}{4}(yy-xx)-\frac{1}{2}xy & \mp\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz \\ \frac{\sqrt{3}}{4}(yy-xx)-\frac{1}{2}xy & \frac{3}{4}xx+\frac{1}{4}yy-\frac{\sqrt{3}}{2}xy & \mp\frac{1}{2}yz\pm\frac{\sqrt{3}}{2}xz \\ \mp\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz & \mp\frac{1}{2}yz\pm\frac{\sqrt{3}}{2}xz & zz \end{bmatrix}, \tag{3}$$

$$T_5=\begin{bmatrix} \frac{1}{4}xx+\frac{3}{4}yy+\frac{\sqrt{3}}{2}xy & \frac{\sqrt{3}}{4}(xx-yy)+\frac{1}{2}xy & \mp\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz \\ \frac{\sqrt{3}}{4}(xx-yy)+\frac{1}{2}xy & \frac{3}{4}xx+\frac{1}{4}yy-\frac{\sqrt{3}}{2}xy & \pm\frac{1}{2}yz\mp\frac{\sqrt{3}}{2}xz \\ \mp\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz & \pm\frac{1}{2}yz\mp\frac{\sqrt{3}}{2}xz & zz \end{bmatrix},$$

$$T_6=\begin{bmatrix} \frac{1}{4}xx+\frac{3}{4}yy-\frac{\sqrt{3}}{2}xy & \frac{\sqrt{3}}{4}(yy-xx)+\frac{1}{2}xy & \pm\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz \\ \frac{\sqrt{3}}{4}(yy-xx)+\frac{1}{2}xy & \frac{3}{4}xx+\frac{1}{4}yy+\frac{\sqrt{3}}{2}xy & \pm\frac{1}{2}yz\pm\frac{\sqrt{3}}{2}xz \\ \pm\frac{\sqrt{3}}{2}yz\mp\frac{1}{2}xz & \pm\frac{1}{2}yz\pm\frac{\sqrt{3}}{2}xz & zz \end{bmatrix}.$$

For simplicity, only the subscripts of the matrix elements have been written down in Eqs. (3). The T matrices have been assumed to be symmetric in the above equations.

When all three of the off-diagonal elements of the T_1 matrix are nonvanishing, then Eqs. (3) (upper signs) predict that the six inequivalent sites become pairwise degenerate at both the a and the b^* axes, and are all degenerate at the c axis. The six sites are nondegenerate in both the (a,b^*) and the (b^*,c) planes, and show up as three pairs of conjugates in the rotation patterns. The six sites are pairwise degenerate in the (a,c) plane, and the (a,c) rotation pattern will show three lines.

If there is disorder in the atomic positions of the sulfate oxygens, and if the disordered oxygens are related to the original oxygens by the three $\{11\bar{2}0\}$ mirror planes or by the three $\langle 11\bar{2}0\rangle$ twofold axes, then the SO_4^- free radicals produced at the disordered sites will be chemically equivalent but magnetically inequivalent from those produced at the original sites. The $\{11\bar{2}0\}$ planes or the $\langle 11\bar{2}0\rangle$ axes are not symmetry operations of the $31m$ point group of the $LiNaSO_4$ lattice, but both are symmetry operations of the underlying crystal lattice. The products of the three σ_d, $\{11\bar{2}0\}$ mirror planes and the six symmetry operations of the $31m$ group $(E,2C_3,3\sigma_v)$ will generate three additional symmetry operations (C_2 and $2C_6$), resulting in the hexagonal C_{6v} group. The C_{6v} group is of the same Laue-symmetry class as the hexagonal D_6 group. Hence, the presence of positional disorder will make the rotation patterns look as if the Laue-class symmetry of the crystal lattice is the hexagonal D_6 symmetry which has 12 symmetry elements. The six additional T matrices are also given in Eqs. (3) (lower signs). When all three of the off-diagonal elements of the T_1 matrix are nonvanishing, then the six disordered sites are degenerate with the six original sites in both the (a,b^*) and the (b^*,c) planes, but are nondegenerate in the (a,c) plane and in any nonmajor crystal plane. When they are nondegenerate, then the six disordered sites and the six original sites will show up as conjugate lines in the rotation patterns.

V. RESULTS AND DISCUSSIONS

The twin-domain patterns of a crystal can be revealed by one or both of the two methods:[37] by observation with a polarizing microscope or by chemical etching. Observations by both methods of our sample crystals does not reveal any twin-domain pattern.

Besides the SO_4^- free radicals, the ESR spectra of the sample crystals also reveal the presence of other free radicals such as SO_3^- and O_3^-, which are the by-products of the further radiolysis of the SO_4^- free radical.[32] We shall report only the analysis of the SO_4^- in this paper. Two orthorhombic SO_4^- centers are detected by ESR at room temperature from pure $LiNaSO_4$ crystals and from $LiNaSO_4$ crystals doped with CrO_4^{2-}. These two centers are designated as center *A* and center *B*. The average *g* values and the anisotropies of center *A* and center *B* indicate that these are the SO_4^- free radicals. The signal intensities of the lines of center *B* are of about 20–30 % of the lines of center *A*. The rotation patterns of center *A* and center *B* in the three major crystal planes are shown in Fig. 2. The T_1 matrix and the principal *g* values and the principal axes of the *g* tensor are listed in Table I. The rotation patterns shown in Fig. 2 are in agreement

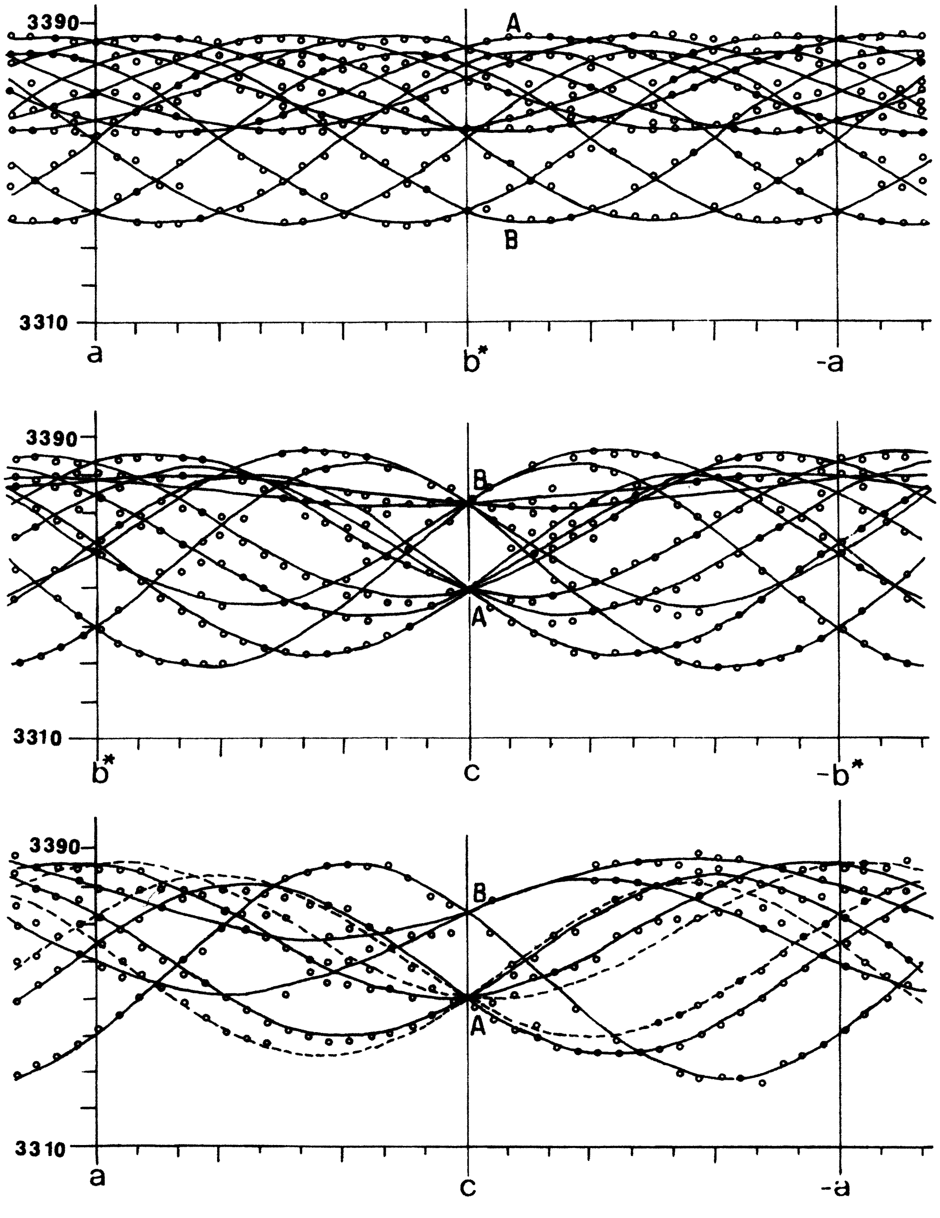

FIG. 2. Rotation patterns of the center *A* and the center *B* of the orthorhombic SO_4^- free radicals in the three major crystal planes. In the (*a*,*c*) plane, lines of center *A* (solid lines) are accompanied by their conjugates (dashed lines), but lines of center *B*, which are weaker, are not accompanied by their conjugates.

with the analysis given in Sec. IV. The lines of center A are accompanied by their conjugates in the (a,c) plane. These conjugate lines are of signal intensities about 10–30% of those of the main lines of center A, depending on the orientation of the magnetic field. The presence of the weak, conjugate lines indicates that there is positional disorder in the sulfate oxygens of the type described in Sec. IV.

Besides center A of the SO_4^- free radical, an intense line with an almost isotropic g value of 1.998 is also detected by ESR at room temperature from crystals doped with Cd^{2+}. The origin of this line is the Cd^+ ion created when the Cd^{2+} ion captures an electron released during radiolysis.[38,39] The hyperfine lines due to the $I=\frac{1}{2}$, Cd^{111} and Cd^{113} isotopes on the high-field side are also detected. From LiNaSO$_4$ crystals doped with Mg^{2+}, very weak orthorhombic lines characteristic of the SO_4^- free radicals are detected by ESR at room temperature, in addition to the center A and center B of the SO_4^- free radicals. Because of their low signal intensities, these lines cannot be analyzed. The lines of center A are observed to be accompanied by their conjugates in both LiNaSO$_4$ crystals doped with Cd^{2+} and Mg^{2+}.

Additional evidence of the existence of positional disorder is provided by the room-temperature rotation pattern of center A in a $(0\bar{1}1)$ plane (referred to the orthorhombic a, $b^*=\sqrt{3}a$, and c unit cell). The result of the analysis of the $(0\bar{1}1)$ pattern is shown in Fig. 3. The sample crystal in this case is LiNaSO$_4$ doped with Cd^{2+}. Besides the almost isotropic spectrum of the Cd^+ ion, the six lines of center A can be identified from the pattern. Center B is of negligible signal intensity in Cd-doped sample crystals. The solid curves shown in Fig. 3 are generated by using T_1 matrix for center A in Eq. (3) (upper signs) and Eq. (1). The fit between the calculated values and the experimental values is quite good, the largest deviation is about 2 G which is about the size of the experimental error incurred by the variation of the resonance frequency induced by the rotation of the sample crystal inside the cavity. The six dashed lines in Fig. 3, which are conjugate to the main lines of center A, are plotted by using the same T_1 matrix for center A in Eq. (3) (lower signs) and Eq. (1).

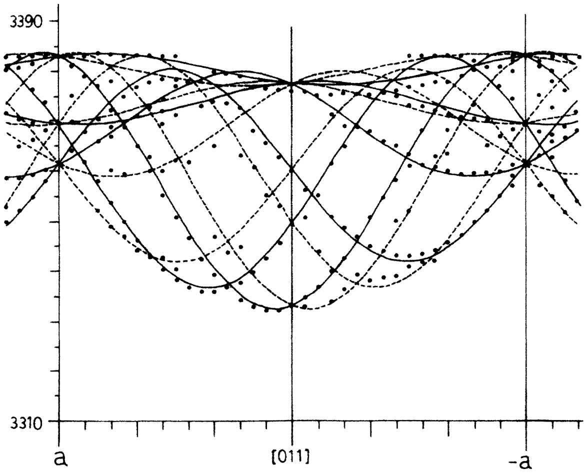

FIG. 3. Rotation pattern of the center A of the SO_4^- free radical in a $(0\bar{1}1)$ plane. The main lines of center A (solid lines) are accompanied by their conjugate lines (dashed lines).

We have also taken the rotation patterns at 200 and 120 K. The ESR of the SO_4^- free radicals does not indicate that LiNaSO$_4$ crystals have a low-temperature structural phase transition between 300 and 100 K. We have also measured the dielectric constant of a c-cut LiNaSO$_4$ crystal between 300 and 120 K, and no anomaly was detected. There is no report in the literature of any low-temperature structural phase transition of LiNaSO$_4$ crystals. Therefore, the changes that we have observed in the ESR spectrum are due to relaxation effects.

The most significant feature of the low-temperature spectrum in pure LiNaSO$_4$ crystals and in LiNaSO$_4$ crystals doped with CrO_4^{2-} is the emergence of a strong and almost isotropic line which we have designated as center D. Center D is of axial symmetry with $g_\parallel=2.018$ and $g_\perp=2.020$. The average g value of center D is 2.019 at 200 K, which is very close to the value of 2.020 for the SO_4^- center in K_2SO_4 at liquid-nitrogen temperature. Hence center D can be identified as a SO_4^- free radical with axial symmetry. The signal intensity of this axial center increases with decreasing temperatures. In LiNaSO$_4$ crystals doped with Cd^{2+}, center D is very weak or nonexistent at low temperatures. Center D is detected at low temperatures in LiNaSO$_4$ crystals doped with Mg^{2+}, but with a reduced signal intensity.

At 200 K, another paramagnetic species designated as center C is also detected to be increasing in signal intensity in pure and CrO_4^{2-}-doped sample crystals. At room temperature, the signals of center C are rather weak, showing only scattered data points in the rotation patterns, and were omitted in Fig. 1. Figure 4 shows the rotation patterns of center C and center D in the three major crystal planes at 200 K. The evaluated parameters for center C and center D are also listed in Table I. At 200 K, the principal values of center C are 2.005, 2.011, and 2.015, and the average value is 2.010. The anisotropy and the average g value of center C are very similar to those reported for the SO_2^- free radical.[20,40] The main lines of center C are also accompanied by their conjugates in the (a,c) plane (see Fig. 4).

At 120 K, another paramagnetic species designated as center E is detected. The signal intensity of center E (which is of orthorhombic symmetry) is much weaker than that of the axial SO_4^- center, and its lines are not accompanied by their conjugates in the (a,c) plane. The evaluated parameters of center E are also listed in Table I. The anisotropy and the average g value of center E are much larger than those normally reported for the SO_4^- free radicals, but center E is still probably a SO_4^- free radical trapped at a different site.

There are four significant experimental facts that we are able to obtain from the ESR of γ-irradiated LiNaSO$_4$ crystals, namely, (1) one of the SO_4^- centers (center A) is accompanied by weak, conjugate lines, (2) the observation of an axial SO_4^- center (center D) having a molecular symmetry identical to its parent SO_4^{2-} radical, (3) the disappearance of the axial SO_4^- center in Cd-doped crystals, and (4) the ESR spectra of the SO_4^- free radical designated as center *A* are identical in pure $LiNaSO_4$ crystals and $LiNaSO_4$ crystals doped with CrO_4^{2-}, Cd^{2+}, and Mg^{2+}.

The mean *g* value of the axial SO_4^- center (center *D*) is typical of the SO_4^- free radicals.[12,18–20] The detection of such an axial SO_4^- free radical whose molecular symmetry is identical to its parent SO_4^{2-} radical would imply that the low molecular symmetry normally observed for the SO_4^- free radicals is not an intrinsic property. Because of the existence of three chemically inequivalent sulfate tetrahedra in a crystal $LiNaSO_4$,[1] it is not easy to identify which one of the three is responsible for the appearance of this axial center. But since the anisotropy of this center is rather small, it is highly probable that it resides on the site of the $(SO_4)_3$ tetrahedron which is almost regular.[1] The disappearance of the axial SO_4^- center in Cd^{2+}-doped crystals is also consistent with the assertion that the low molecular symmetry usually observed for the SO_4^- free radicals is not an intrinsic property. It is most likely that the Cd^{2+} ions replace the Na^+ ions, since their ionic radii are identical. In such a case, Na^+ vacancies will be created as a charge-compensation mechanism, and this can explain the disappearance of the axial SO_4^- center. The ESR signal intensity of center *A* is stronger in $LiNaSO_4$ crystals doped with Cd^{2+} than in the three other types of the sample crystals, and this seems to suggest that center *A* is produced at the $(SO_4)_3$ site, and that

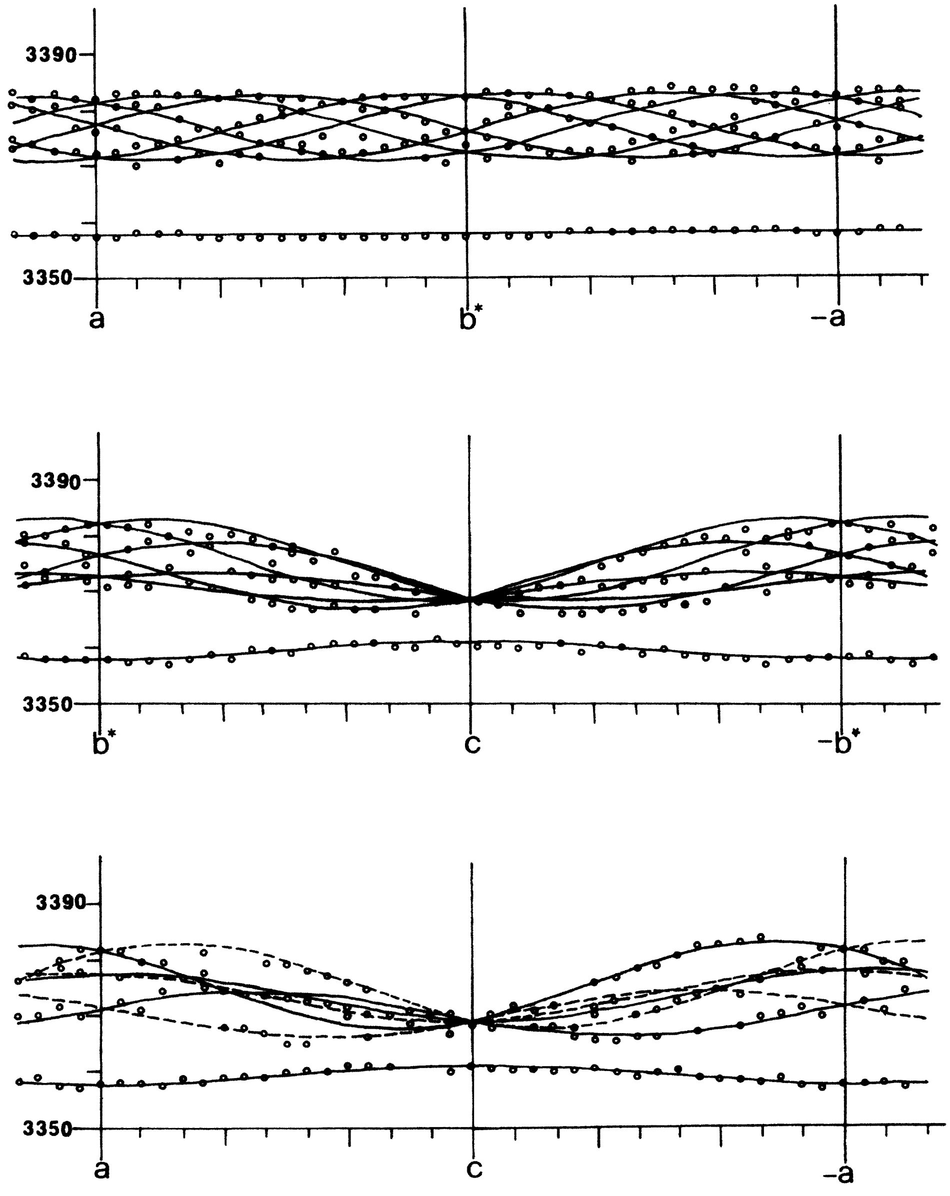

FIG. 4. Rotation patterns at 200 K of center *C* which is of orthorhombic symmetry and which is probably the SO_2^- free radical and the axial SO_4^- free radical (center *D*) in the three major crystal planes. In the (a,c) plane, lines of center *C* (solid lines) are accompanied by their conjugate lines (dashed lines).

it is associated with a local Na^+ vacancy. The fact that center *A* of the SO_4^- free radicals is observed to be identical in all samples crystals, pure and doped, would imply that the Na^+ vacancy is mainly produced by radiation damage.

VI. CONCLUSIONS

We have established through the ESR of the SO_4^- free radicals in $LiNaSO_4$ crystals that a fraction of the sulfate groups is positionally disordered, and the positions of the disordered sulfate oxygens are probably related to the main oxygens by the $\{11\bar{2}0\}$ mirror reflections or by the twofold $\langle 11\bar{2}0\rangle$ axes. Since the sample crystals are not observed to be composed of twin domains, it can be concluded that the disorder is distributed randomly and uniformly throughout the crystal lattice. We have also established that the orthorhombic SO_4^- centers in $LiNaSO_4$ crystals are probably associated with Na vacancies created by radiation damage, and that the lowering of the magnetic and the molecular symmetry of the SO_4^- free radicals is not an intrinsic property.

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[1] B. Morosin and D. L. Smith, Acta Crystallogr. **22**, 906 (1967).

[2] D. Teeters and R. Frech, J. Chem. Phys. **76**, 799 (1982).

[3] D. Teeters and R. Frech, Phys. Rev. B **26**, 4132 (1982).

[4] R. Frech and D. Teeters, J. Phys. Chem. **88**, 417 (1984).

[5] H. Schulz, U. Zucker, and R. Frech, Acta. Crystallogr. B **41**, 21 (1985).

[6] S. Bhakay-Tamhane, A. Sequira, and R. Chidambaram, Acta Crystallogr. C **40**, 1648 (1984).

[7] M. Karppinen, J. O. Lundgren, and K. Liminga, Acta Crystallogr. C **39**, 34 (1983).

[8] P. A. Sandomirskii, S. S. Meshalkin, and I. V. Rozhdestvenkaya, Kristallografiya **28**, 67 (1983) [Sov. Phys.—Crystallogr. **28**, 33 (1983)].

[9] N. S. Dalal, C. A. McDowell, and R. Srinivasan, Phys. Rev. Lett. **25**, 823 (1970).

[10] T. Kawano, K. Niimori, K. Hukuda, and N. Fujita, J. Phys. Soc. Jpn. **29**, 633 (1970).

[11] R. D. Truesdale, H. A. Farach, and C. P. Poole, Jr., Phys. Rev. B **22**, 365 (1980).

[12] J. T. Yu and S. Y. Chou, J. Phys. Chem. Solids **47**, 1171 (1986).

[13] Y. Shiroishi, A. Nakata, and S. Sawada, J. Phys. Soc. Jpn. **40**, 911 (1976).

[14] H. Ozeki and A. Sawada, J. Phys. Soc. Jpn. **51**, 2047 (1982).

[15] W. A. Dollase, Acta Crystallogr. B **25**, 2298 (1969).

[16] S. J. Chung, Ph. D. Thesis, Technische Hochschule Aachem, 1972.

[17] V. V. Gromov and J. R. Morton, Can. J. Chem. **44**, 527 (1966).

[18] J. R. Morton, D. M. Bishop, and M. Randic, J. Chem. Phys. **45**, 1885 (1966).

[19] K. Aiki and K. Hukuda, J. Phys. Soc. Jpn. **22**, 663 (1967).

[20] N. Hariharan and J. Sobhanadri, Mol. Phys. **17**, 507 (1967).

[21] A. A. Alybakov, V. M. Bujko, and K. Sharsheev, Crystal Res. Technol. **16**, 617 (1981).

[22] F. Holuj and F. Drozdowski, Ferroelectrics **36**, 379 (1981).

[23] C. H. A. Fonseca, G. M. Ribeiro, R. Gazzineli, and A. Chaves, Solid State Commun. **46**, 221 (1983).

[24] J. T. Yu, Solid State Commun. **62**, 109 (1987).

[25] P. W. Atkins, J. A. Brivati, A. Horsfield, M. C. R. Symons, and P. A. Trevalion, in Proceedings of the 6th International Symposium on Free Radicals, Cambridge, 1963.

[26] P. W. Atkins, M. C. R. Symons, and H. W. Wardale, J. Chem. Soc. 5215 (1964).

[27] V. A. Zeman and J. Zeman, Acta Crystallogr. **10**, 409 (1957).

[28] A. J. Bradley, Philos. Mag. **49**, 1225 (1925).

[29] K. Okada and J. Ossaka, Acta Crystallogr. B **36**, 919 (1980).

[30] G. Lehmann, Crystal Res. Technol. **18**, K75 (1983).

[31] A. A. Alybakov, V. M. Bujko, and K. Sharsheev, Cryst. Res. Technol. **18**, K77 (1983).

[32] B. V. R. Chowdari and Y. Ravi Sekhar, J. Chem. Phys. **75**, 1074 (1981).

[33] S. V. Bhat, N. C. Mishra, and R. Srinivasan, J. Phys. Chem. Solids **43**, 1157 (1982).

[34] H. A. Farach and C. P. Poole, Jr., Adv. Magn. Reson. **5**, 229 (1971).

[35] N. M. Atherton, *Electron Spin Resonance* (Wiley, New York, 1973).

[36] J. A. Weil, T. Buch, and J. E. Clapp, Adv. Magn. Reson. **6**, 183 (1973).

[37] M. J. Buerger, *Crystal-structure Analysis* (Wiley, New York, 1966).

[38] V. F. Krutikov, N. I. Silkin, and V. G. Stepanov, Fiz. Tverd. Tela (Leningrad) **13**, 3100 (1971) [Sov. Phys.—Solid State **13**, 2601 (1972)].

[39] T. Toyotomi and R. Onaka, J. Phys. Soc. Jpn. **34**, 623 (1973).

[40] P. W. Atkins, A. Horsfield, and M. C. R. Symons, J. Chem. Soc. 5220 (1964).